ENTHALPIES OF FORMATION OF DIBUTYL PHTHALATE AND METHYL 4-HYDROXYBENZOATE[1]

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ABSTRACT

Enthalpies of formation of liquid dibutyl phthalate (DBP, -864.67±4.77 kJ·mol^{-1}) and crystalline methyl 4-hydroxybenzoate (4-MHB, -562.20±2.29 kJ·mol^{-1}) were determined by combustion calorimetry. Relations of these values to the structures of the molecules are discussed.

KEY WORDS: combustion calorimetry; dibutyl phthalate; enthalpy of formation; methyl 4-hydroxybenzoate

1. INTRODUCTION

Knowledge accumulated on enthalpies of formation of organic compounds is vitally important for many scientific and practical applications, but often needs careful critical assessment and additional experimental validation. A case is aromatic esters used as plasticizers, repellents, food preservatives, and intermediates in synthesis of plastic materials. Thermodynamics of processes with their participation, their environmental and health impact are widely discussed. In spite of the existence of many experimental values of enthalpies of formation reported for n-alkyl phthalates (Table I), they are neither reliable nor consistent (Fig. 1). Regular changes in the homologous series of phthalates are not clear, making any prediction doubtful. Even assessed recommended values [10] are not accompanied by realistic uncertainties.

Experimental measurement of the enthalpy of combustion for liquid dibutyl phthalate (DBP) should provide a reliable checkpoint in the series of phthalates and verify an earlier evaluation [11]. From a scientific point of view, it is interesting to explore the effect of the interaction between the substituents in the 1 and 2 positions of the benzene ring on the CH_2 group increment in the enthalpy of formation (-25.3±0.5 $kJ \cdot mol^{-1}$), which is nearly constant for different classes of compounds in the liquid state (alkanes, alcohols, ketones, acids, esters, etc.)

A similar measurement for crystalline methyl 4-hydroxybenzoate (4-MHB) combined with the known value for its isomer, 4-methoxybenzoic acid, provides the enthalpy effect associated with the migration of the methyl group from the ester to ether position.

2. MEASUREMENTS

2.1. Materials

Commercial dibutyl phthalate $C_{16}H_{22}O_4$ (Aldrich) with a stated purity of 99% was twice distilled at 800 Pa in a 1.2 m packed column and dried over 4A type molecular sieves. Prior to the combustion experiments, it was stored in a desiccator over P_2O_5 during a week. The final purity was 99.92 mass % (g.l.c., steel column 3 m × 3 mm filled with DS 550, carrier N_2, FID, sampling temperature 463 K, column temperature 433 K). The molecular mass used was 278.34348. The liquid density at T=289.15 K 1049 $kg \cdot m^{-3}$ was calculated with a published equation [12].

Commercial methyl 4-hydroxybenzoate $C_8H_8O_3$ (Fluka) with a stated purity of 99 % was crystallized from ethanol and a mixture of isooctane with acetone, dried in a vacuum at 6 Pa until constant mass, and kept in darkness in a desiccator over anhydrous magnesium perchlorate. G.l.c. analysis (steel column 2 m × 3 mm filled with OV-1 on Chromaton-N-Super, carrier N_2, FID, sampling temperature 473 K, temperature program 373 K (10 min), 463 K (30 min)) showed the purity to be 99.93 mass %. The molecular mass used

was 152.14732. The crystal density 1384±1 $kg \cdot m^{-3}$ at T=294.15 K was measured in a pycnometer using water as an auxiliary liquid.

2.2. Experimental Procedure

The energy of combustion was measured in three isoperibolic calorimeters V-08MA described earlier [13] with static bombs A, B, and C, calibrated with benzoic acid (D. Mendeleev Institute of Metrology, St. Petersburg, bomb energy of combustion -26434.4 $J \cdot g^{-1}$ for mass in vacuum). Calorimeter constants were W(A) = 14892.0 ± 5.4, W(B) = 14939.4 ± 6.5, and W(C) = 14955.7 ± 5.6 $J \cdot K^{-1}$ for 95% level of confidence. DBP was placed in polyethylene bags (density 946 $kg \cdot m^{-3}$, bomb energy of combustion -46435.1±6.8 $J \cdot g^{-1}$). Pellets of 4-MHB were burned in PET bags (density 1380 $kg \cdot m^{-3}$, bomb energy of combustion -22879.7 ±11.2 $J \cdot g^{-1}$). The energy of ignition was 2.0 J in all cases.

3. RESULTS AND DISCUSSION

Primary experimental results are given in Table II. Uncertainties are calculated following published recommendations [14] and are represented in accordance with the schema described recently [15]. Device specification in the form of calibration uncertainty was propagated to the total heat effect of an experiment and divided by the sample mass, average values being 14.3 $J \cdot g^{-1}$ for DBP and 11.9 $J \cdot g^{-1}$ for 4-MHB. Repeatability for 95 % level of confidence was 4.6 $J \cdot g^{-1}$ for DBP and 5.5 $J \cdot g^{-1}$ for 4-MHB. For calculation of the expanded uncertainty, the contribution of the auxiliary substances and impurities were also considered. It was assumed that the massic energy of combustion of the impurities differs from the main compounds by 10%. Expanded uncertainties of the enthalpies of combustion were 15.2 $J \cdot g^{-1}$ for DBP and 13.2 $J \cdot g^{-1}$ for 4-MHB.

Combined expanded uncertainties for 95% level of confidence were calculated by propagation of the uncertainty of the nominal conditions of the reactions (298.15 K and 101.325 kPa) estimated as 10% of Washburn correction. They are 15.3 $J \cdot g^{-1}$, or 4.27 $kJ \cdot mol^{-1}$ for DBP and 13.4 $J \cdot g^{-1}$, or 2.03 $kJ \cdot mol^{-1}$ for 4-MHB. Enthalpies of formation were calculated using the reference values $\Delta_f H°(H_2O, l)$ = 285.83±0.04 $kJ \cdot mol^{-1}$ and $\Delta_f H°(CO_2, g)$ = 393.51±0.13 $kJ \cdot mol^{-1}$ [16]. Thermochemical characteristics of combustion and formation of DBP and 4-HMB are given in Table III.

The enthalpy of formation of liquid dibutyl phthalate is the third reliable reference point for phthalates, in addition to dimethyl phthalate [2, 3] and diethyl phthalate [4]. Its value is close to the earlier recommendation [11] (870 $kJ \cdot mol^{-1}$) and discards the preceding recommendation [10] (842.6 $kJ \cdot mol^{-1}$), as well as the additivity employed there (calculated value -900.9 $kJ \cdot mol^{-1}$).

Reliable experimental values of the enthalpies of formation of dimethyl, diethyl, and dibutyl phthalates along with the not proven values for dipentyl and dioctyl phthalates are compared with the enthalpies of formation of 1-alkanols in Fig. 2. The values for the phthalates are reduced to one alkyl group by dividing by 2. All values are relative, with values shown as differences from that for the first member in each series; dimethyl phthalate and methanol, respectively. Therefore, the plot shows successive increases in the absolute values of the enthalpy of formation with insertion of CH_2 groups. Alcohols show behavior common for many different classes of compounds with a larger initial increment followed by a nearly constant increment. The alcohols are the closest to the phthalate class of chemical compounds R-O-X, for which accurate enthalpies of formation are known for a sufficient range of alkyl R size. The data for esters and ethers are either too few or not reliable.

In the case of phthalates, insertion of the first CH_2 group (transition from methyl to ethyl phthalate) is also accompanied by a larger enthalpy effect than insertion of subsequent CH_2 groups. The average effect of insertion of the two next CH_2 groups (from ethyl to butyl phthalate), -27.9 $kJ \cdot mol^{-1}$per CH_2 group, is a bit larger than the generalized value (-25.3±0.5 $kJ \cdot mol^{-1}$), which suggests the absence of additional strain in longer alkyl chains in phthalates. The known experimental values for dipentyl phthalate and dioctyl phthalate are not accurate. Apparently, the first is overestimated, and the second is underestimated in terms of absolute values. Addition of the universal CH_2 group increment to the enthalpy of formation of dibutyl phthalate seems to be the best way to predict enthalpies of formation for higher phthalates.

The enthalpy of formation of methyl 4-hydroxybenzoate is determined here for the first time. It is nearly equal to that of 4-methoxybenzoic acid (-561.7±1.3 $kJ \cdot mol^{-1}$) [17] suggesting zero enthalpy effect associated with migration of the CH_3 group from the ester to the ether position.

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Table I. Literature experimental data on the enthalpies of formation of liquid n-alkyl phthalates at T=298.15 K

Compound	$\Delta_f H°(298.15)$	Source	Comment
Dimethyl phthalate	-662.3	Ref. 1	Without Washburn corrections
	-683.8±2.7	Ref. 2	
	-684.28±2.48	Ref. 3	
Diethyl phthalate	-757.41±2.22	Ref. 4	
	-777±12	Ref. 5	Revised by Cox and Pilcher [6]
	-638	Ref. 7	Without Washburn corrections
Dibutyl phthalate	-778	Ref. 8	Without Washburn corrections
	-843±13	Ref. 9	Revised by Cox and Pilcher [6]
Dipentyl phthalate	-924±13	Ref. 9	Revised by Cox and Pilcher [6]
Dioctyl phthalate	-1036.	Ref. 1	Without Washburn corrections

Table II. Experimental results of combustion of DBP and 4-MHB

m g	m_{aux} g	ΔT K	q_{HNO3} J	q_{aux} J	$q_{Washburn}$ J	Bomb	$-\Delta_c U°$ $J \cdot g^{-1}$
Dibutyl phthalate							
0.49991	0.04067	1.15741	3.3	1888.5	8.2	B	30783.5
0.39961	0.04431	0.96475	2.4	2057.5	6.5	A	30776.6
0.53113	0.04485	1.23850	3.0	2082.6	8.8	A	30780.7
0.40464	0.04055	0.96025	3.3	1882.9	6.5	B	30770.2
0.46912	0.04915	1.12021	3.6	2282.3	7.8	B	30780.4
Methyl 4-hydroxybenzoate							
0.55033	0.02767	0.94896	2.1	633.1	9.8	A	24503.5
0.46516	0.02597	0.80583	1.8	594.2	8.2	A	24495.3
0.51645	0.02998	0.89321	2.4	685.9	9.2	C	24511.7
0.49311	0.02983	0.85429	2.1	682.5	8.8	C	24500.0
0.51510	0.02840	0.89200	2.4	649.8	9.1	A	24500.8

m	sample mass
m_{aux}	mass of the auxiliary substance (PE for DBP and PET for 4-HMB)
ΔT	corrected temperature rise
q_{HNO3}	energy of formation of nitric acid
q_{aux}	energy of combustion of the auxiliary substance
$q_{Washburn}$	sum of Washburn corrections
$-\Delta_c U°$	standard energy of combustion

Table III. Thermochemical characteristics of combustion and formation of DBP (l) and 4-HMB (cr) at T=298.15 K and P = 101.325 kPa along with their combined expanded uncertainties.

	DBP	4-MHB
Standard energy of combustion ($J \cdot g^{-1}$)	-30778.3±15.3	-24502.3±13.4
Standard energy of combustion ($kJ \cdot mol^{-1}$)	-8566.94±4.27	-3727.96±2.03
Standard enthalpy of combustion ($kJ \cdot mol^{-1}$)	-8575.62±4.27	-3729.20±2.03
Standard enthalpy of formation ($kJ \cdot mol^{-1}$)	-864.67±4.77	-562.20±2.29

Figure Captions

Fig. 1. Literature experimental data on the enthalpies of formation of liquid n-alkyl phthalates at 298.15 K.

Fig. 2. Selected relative enthalpies of formation of liquid n-alkyl phthalates at 298.15 K reduced to 1 alkyl group -HF = -1/2 [$\Delta_f H°$ - $\Delta_f H°$(dimethyl phthalate)] compared with relative enthalpies of formation of liquid 1-alkanols -HF = -[$\Delta_f H°$ - $\Delta_f H°$(methanol)]. ● - phthalates, ○ - alcohols.

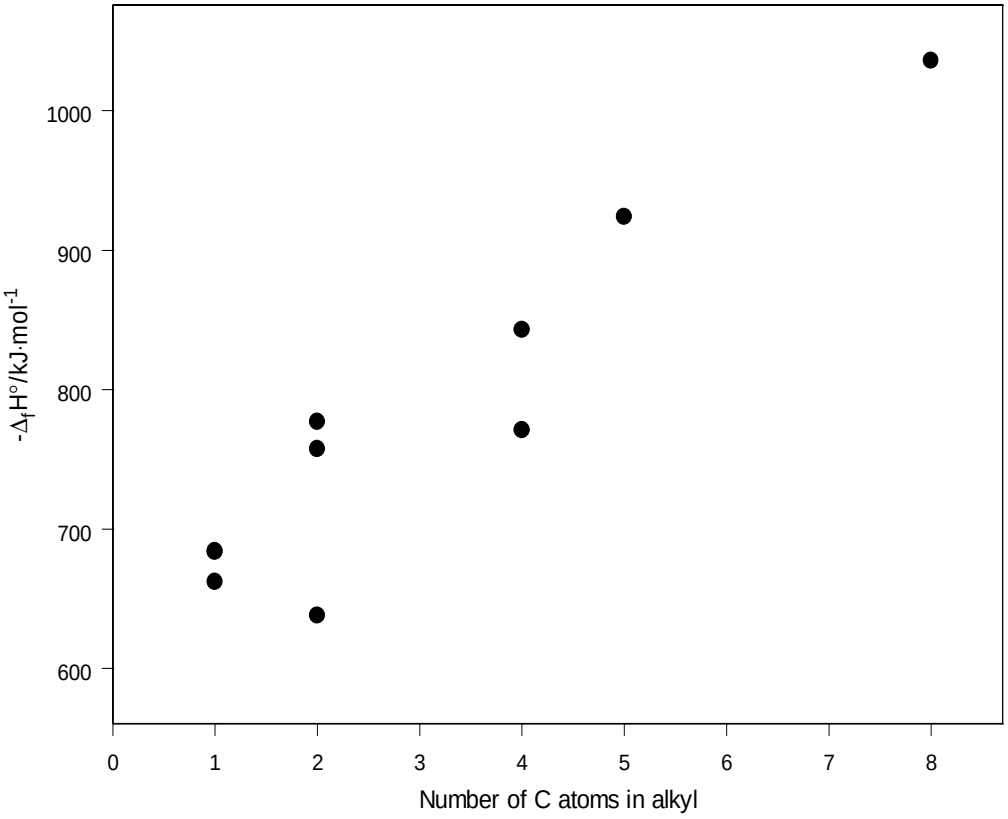
1000
900
800
700
600
-ΔfH°/kJ·mol-1
0
1
2
3
4
5
6
7
8
Number of C atoms in alkyl

Fig. 1

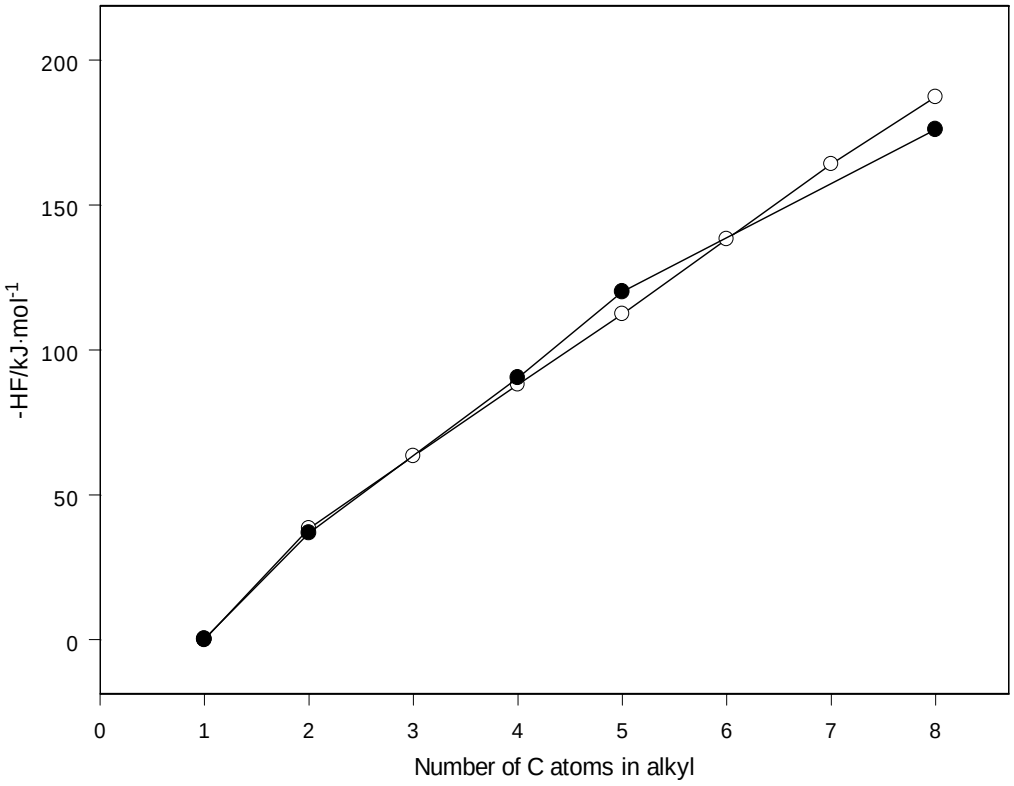
200
150
100
50
0
-HF/kJ·mol-1
0
1
2
3
4
5
6
7
8
Number of C atoms in alkyl

Fig. 2